I. SOLUBILITY IN MIXED SOLVENTS

II. THERMODYNAMICS OF DILUTE HIGH POLYMER SOLUTIONS

BY

PATRICIA McMILLIN SAXTON

B. A., Radcliffe College, 1950
M. S., University of Illinois, 1952

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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PART I. SOLUBILITY IN MIXED SOLVENTS

The influence of van der Waals forces on the solvent power of liquids can be used to obtain qualitatively good guides in the choice of mixed solvents for a substance difficultly soluble in single solvents.

The Henry's law constants, and hence the solubilities of a substance in single or mixed solvents are expressed in terms of the van der Waals constants (a and b) through calculations of the vapor pressures of liquids in binary or ternary mixtures. Comparison of these Henry's law constants indicates when a substance will be more soluble in a given mixture of solvents than in the individual solvents.

In terms of intermolecular attractions, a substance will show enhanced solubility in the mixed solvents if it exhibits approximately the same behavior in the individual solvents (i.e., if $a_{ij}/\sqrt{a_i a_j} \simeq a_{ik}/\sqrt{a_i a_k}$), and in addition the mixture of solvents obeys the condition $a_{jk}/\sqrt{a_j a_k} < 1$. If the intermolecular attractions are ideal, enhanced solubility may be expressed in terms of $\sqrt{a_i}/b_i$ or, what is almost equivalent, the solubility parameters, δ_i. Gee[1] and Scott[2] have given as a necessary, but not sufficient condition for enhanced solubility, $\delta_j > \delta_i > \delta_k$. As a result of our calculations, we can state the more rigid necessary and sufficient condition for enhanced solubility in mixed solvents,

$$\delta_j + \frac{x_k b_k}{2(x_j b_j + x_k b_k)}(\delta_k - \delta_j) > \delta_i > \delta_k + \frac{x_j b_j}{2(x_j b_j + x_k b_k)}(\delta_j - \delta_k)$$

PART II. THERMODYNAMICS OF DILUTE HIGH POLYMER SOLUTIONS

The energy of mixing of an infinitely dilute high polymer solution in terms of van der Waals forces and the radius of an equivalent polymer sphere can be derived by considering the various types of interactions taking place in the solution between polymer segments and solvent molecules. The first approximation to this energy of mixing, which is simply the van der Waals energy

of the equivalent polymer spheres plus the van der Waals energy of the solvent molecules outside the polymer spheres, is found to be quite accurate.

This expression for the energy of mixing is combined with Flory's[3] and Wall's[4] expressions for the entropy to form the free energy, which, when minimized, gives an implicit expression for the thermodynamic equilibrium value of the radius of the equivalent polymer sphere in an infinitely dilute solution. The conditions under which a polymer will tend to expand in solution are the same as those found in the solubility studies for a simple solute to be more soluble in a given solvent; that is, $a_{ij}/\sqrt{a_i a_j} > 1$. By various methods of successive approximations, explicit equations can be obtained for values of the radius large or small compared with the radius in pure polymer.

Further approximate calculations show that interactions between polymer molecules or small amounts of overlapping of polymer molecules have a negligible effect on the equilibrium radius of the polymer spheres in actual dilute solutions.

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VITA

Patricia McMillin Saxton was born on August 8, 1928, in Washington, D.C. After graduating from Boulder High School at Boulder, Colorado, in 1946, she entered Radcliffe College at Boston, Massachusetts. She received the degree of Bachelor of Arts, summa cum laude, from that institution in 1950. She entered the Graduate College of the University of Illinois in 1950, and received the degree of Master of Science in 1952.

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